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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

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POLYMER LETTERS VOL. 1, PP. 65-66 (1963)

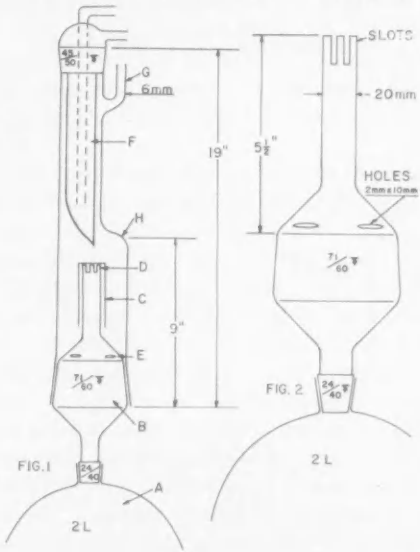
CONTROL OF DUST IN LIQUIDS FOR LIGHT-SCATTERING STUDIES

The problem of eliminating dust from light-scattering cells or other vessels which are used to store centrifuged or filtered dust-free solvent or solutions is a major one, especially in those cases where the centrifuge cell and light-scattering cell are not one and the same. The apparatus described below has been found to be extremely helpful in preparing dust-free glassware.

A relatively elaborate unit for cleansing glassware of dust has been described by Thurmond (1). The apparatus described here is much simpler in construction, less expensive, and not prone to breakage. In addition, the glassware to be cleansed is automatically dried in the apparatus.

The cell or glassware to be cleansed should be free of polymer prior to being put into the washer. Trichloroethylene has been found to be the most efficient liquid for dust removal.

A two liter round-bottom flask, A (Fig. 1), acts as a boiling pot. Solvent vapors rise through the $\overline{\$}$ 71/60 joint, B (Fig. 1), to wash the in-



Figs. 1 and 2. A = Two-liter round-bottom flask. B = $\overline{\$}$ 71/60 joint. C = Light-scattering cell. D = Slotted tube. E = The holes above the $\overline{\$}$ 71/60 ground glass joint through which the vapors rise and condense. F = Coldfinger. G = Sidearm tubing for venting. H = Outer jacket.

side of the cell, C (Fig. 1), which rests in an inverted position on the slotted tube, D (Fig. 1). Additional vapors rise through the holes, E (Fig. 1), just above the ground glass joint ($\overline{\$}$ 71/60) to wash the outside of the cell. These holes also act as the passageway for condensate to return to the pot.

The centerpiece tube, with the $\overline{\$}$ 71/60 joint, from the boiler to the cell, is shown schematically in Figure 2.

The coldfinger, F (Fig. 1), acts in a twofold manner. It first condenses the vapors outside the cell and then this distillate drips onto the bottom of the inverted cell. This, in turn, causes condensation of vapors inside the cell which acts to thoroughly cleanse the cell of dust. After approximately 5 min. of washing action, heat to the boiler is stopped and the residual heat is sufficient to dry the cell. Venting is necessary through sidearm tubing, G (Fig. 1), to prevent a closed system.

The jacket, H (Fig. 1), can be removed and a cap placed over the inverted cell before any dust can be deposited.

Thanks are due to the management of FMC Corporation for permission to publish this note.

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(1) Thurmond, C. D., J. Polymer Sci., 8, 607 (1952).

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POLYMER LETTERS VOL. 1, PP. 67-71 (1963)

ISOTACTIC CIS-1,4 POLY(1,3-PENTADIENE)

It was foreseeable that cis-1,4 polymers of 1,3-pentadiene, owing to the presence of an asymmetric carbon atom in each monomeric unit, could exist in different stereoisomeric structures; e.g., isotactic, syndiotactic, atactic. Of these possible stereoisomers only the syndiotactic cis-1,4 polypentadiene was known until now (1).

We have recently obtained a new cis-1,4 polymer of 1,3-pentadiene which, on the basis of x-ray analysis, appears to have an isotactic structure of the asymmetric carbon atoms. The new polymer was obtained with the aid of catalysts prepared from $Al(C_2H_5)_3$ and a titanium tetraalkoxide (Al/Ti from 3 to 10) in hydrocarbon solvents.

In a typical run 15 ml. of the trans isomer (99% pure) of 1,3-pentadiene were introduced into a catalyst solution, prepared by reacting at ordinary temperature 0.6 ml. of titanium tetra n-butoxide with 1.8 ml. of $Al(C_2H_5)_3$ in 80 ml. of anhydrous benzene.

After 15 hr. of polymerization at about 0°C. 3 g. of polymer were obtained. In order to remove the less stereoregular low molecular weight macromolecules the crude polymerization product was repeatedly dissolved in benzene and reprecipitated with methyl ethyl ketone; after 3 dissolutions and reprecipitations a polymer was obtained, highly crystalline to x-ray, having m.p. ~44°C. (polarizing microscope) and $[\eta]$ 7 dl./g. (in toluene at 30°C.).

The prevailingly cis-1,4 enchainment of the new polymer is revealed by the presence in the I.R. spectrum of the molten or dissolved polymer (Fig. 1, solid line) of an intense band at about 13.3 μ, characteristic of the cis internal double bonds; far less intense bands are present at 10.35 μ, (trans internal double bonds) and at 11 μ (vinyl groups).

By assuming, as absorption coefficients for the bands at 10.35, 11, and 13.3 μ, the values of 10×10^4, 12×10^4, and 6×10^4 moles^{-1}cm.$^{-1}$ml. (2), respectively, we have calculated a cis-1,4 content of 85-90% for the polymer we have isolated. Such a value might be slightly modified when an improved method of analysis is available.

The I.R. spectrum of the new polymer in the crystalline state (Fig. 1, dashed line) shows new bands with respect to the spectrum of the molten or dissolved polymer, the most intense of which are at 13.40, 11.85, 10.80, 9.95 μ, while others, less intense, are at 8.85, 8.99, 8.15, 7.60, 6.91 μ.

With regard to the differences between the I.R. spectra of the isotactic and the syndiotactic cis-1,4 polypentadienes, these appear small in the spectra of the dissolved or molten polymers, whereas they appear noticeable in the spectra of the two polymers in the crystalline state.

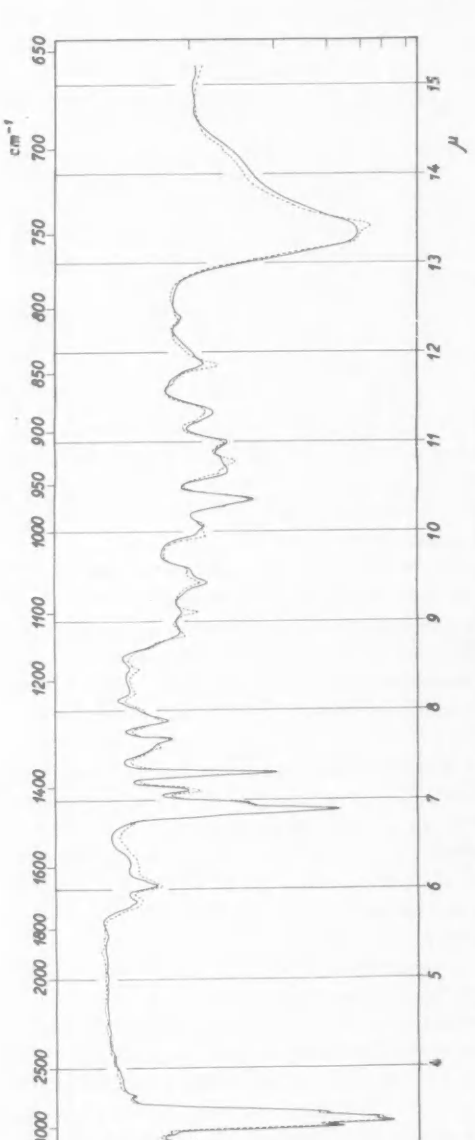

Fig. 1. I.R. spectra of a sample of cis-1,4 isotactic polypentadiene in the solid state (dashed line) and in the molten state (solid line).

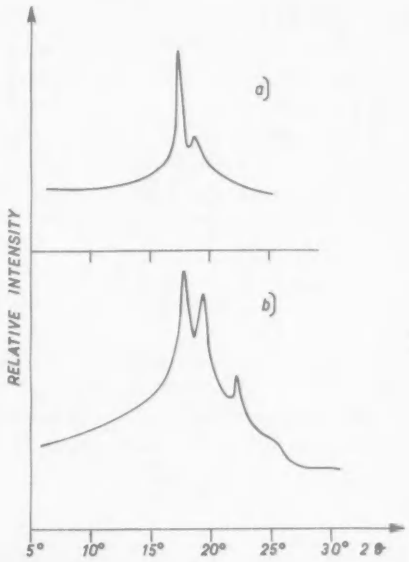

Fig. 2. X-ray powder spectra (CuKα), registered with a Geiger counter, of samples of cis-1,4 polypentadienes: (a) isotactic, (b) syndiotactic.

Noteworthy in the spectra of the two polymers in the crystalline state is the different position of the band of the cis double bonds, which is at about 13.2 μ in the case of the syndiotactic and at about 13.4 μ in that of isotactic polymer (whereas in the spectra of the molten or dissolved polymers this band is at about 13.3 μ both for isotactic and syndiotactic polypentadiene).

The structural regularity of the new polymer, which is revealed by the differences between the I.R. spectra of the solid and the molten polymer, is also confirmed by the x-ray spectrum, which shows the presence of a crystalline structure. From the examination of the x-ray Geiger spectrum (Fig. 2a), it has been observed that the most intense maxima correspond to layer distances d = 5.17 and 4.71 A; such distances are very close to those observed for the most intense maxima of the syndiotactic polymer (Fig. 2b), but the ratios between the corresponding diffraction intensities are different in the two polymers.

From the fiber spectrum of the new polymer an identity period of about 8.15 ± 0.05 A. was measured, which is slightly smaller than that of the syndiotactic polymer (8.50 ± 0.05 A.). In a previous communication (1) on the basis of a conformational analysis of the chains of the

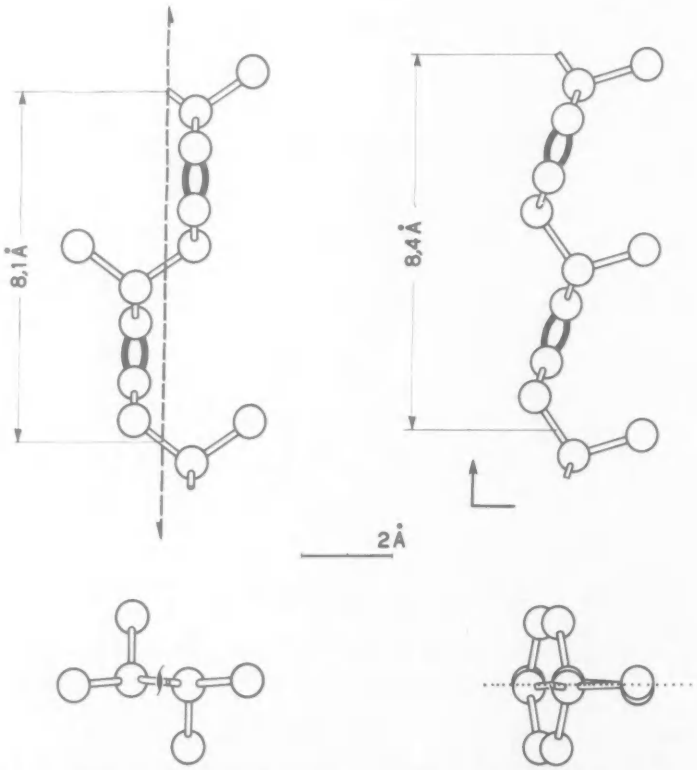

Fig. 3. Chain models of the cis-1,4 isotactic (left) and the cis-1,4 syndiotactic polypentadienes.

cis-1,4 polypentadienes, we foresaw that the identity period of the cis-1,4 isotactic polypentadiene, at that time unknown, could have been about 8.1 A., which is very close to that actually found. We assume, therefore, for the cis-1,4 isotactic polypentadiene in the crystalline state, a chain model shown in Figure 3, already reported in our previous communication (1). Such a model is characterized by the presence of a screw twofold axis, while the chain model of the cis-1,4 syndiotactic polypentadiene is characterized by a glide plane (1).

The isotactic structure of the new polymer is further confirmed by the behavior of the x-ray diffracted intensity on the non equatorial layers of the fiber spectrum. In the spectrum of the isotactic polymer the amount of the total intensity diffracted on the first layer is about the same as that on the 2nd, whereas in the spectrum of syndiotactic polymer it is much lower, as already reported (1). Also the total intensity diffracted

on the 3rd layer is higher for the isotactic than for the syndiotactic polymer. Such data can be interpreted by taking into account that, in the syndiotactic model, six among the carbon atoms which constitute the repetition unit are nearly superimposed along the direction of the chain axis at a distance of c/2 (c = identity period) and cannot therefore appreciably contribute to the diffraction on the layers characterized by an odd l index; this does not occur in the case of isotactic polymer.

The two cis-1,4 polymers of 1,3-pentadiene constitute the first example of ditactic polymers, obtained from the same diolefinic monomer, with respectively isotactic and syndiotactic structure.

The elastomeric properties of the new polymer, which appear interesting, will be reported in a subsequent communication.

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(1) Natta, G., L. Porri, A. Carbonaro, F. Ciampelli, and G. Allegra, Makromol. Chem., 51, 229 (1962).

(2) Average values taken from the literature. See, for example, H. L. McMurray and V. Thornton, Anal. Chem., 24, 318 (1952).

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COPOLYMERIZATION REACTIVITY RATIOS ACRYLIC AND METHACRYLIC ACIDS WITH BUTYL ACRYLATE AND BUTYL METHACRYLATE

The purpose of this note is to report the measurement of copolymerization reactivity ratios for acrylic and methacrylic acids each with n-butyl acrylate and n-butyl methacrylate. The recent comprehensive compilation by Young (1) of r_1, r_2, and Q-e values for a multitude of monomers does not include the copolymerization of either of these acids with a corresponding ester, nor of an acrylate with the corresponding methacrylate. The present results show that in each case the acid monomer lags slightly behind its ester in copolymerization. The two cases of acrylate-methacrylate copolymerization agree very well if a small correction for the acid lag is applied.

Experimental Details

Inhibited glacial acid monomers were purified by fractional crystallization in ice; assay by base titration indicated purity of 96% for acrylic acid and 98% for methacrylic acid. Butyl acrylate and butyl methacrylate were purified by distillation under reduced pressure. Monomers were stored at −20°C. until use.

Polymerizations were carried out in capped 8 oz. bottles at 50°C., using 20 g. total monomers, 40 g. ethyl alcohol as solvent, and 0.1 g. benzoyl peroxide catalyst. Final conversions varied between 5 and 14%.

Polymers were purified of unreacted monomers by dialysis in Visking cellophane tubing against about three volumes of ethyl alcohol. Titrations of the extracts with base showed that residual acid monomer was negligible after five or six extractions; presumably the extraction of ester monomer was similarly efficient. The dialyzed polymer solution was titrated with base to determine acid content. As soon as some of the acid had been saponified, it was possible to add enough water, without precipitating polymer, to obtain a sharp endpoint, which occurred at pH 9 to 10. Polymer compositions were calculated from the titrations and the total polymer content of the solutions. Reactivity ratios were calculated by the method of Fineman and Ross using weight-fraction compositions.

Results

The copolymer composition curves are shown in Figure 1. Table I lists the monomer and polymer compositions, the experimental reactivity

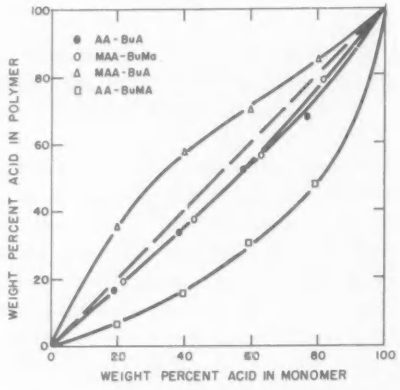

Fig. 1. Copolymer composition curves.

TABLE I

Monomer and Polymer Compositions and Reactivity Ratios

Per cent acid		Exptl.		Calc. (1)	
Monomer	Polymer	r_1	r_2	r_1	r_2
	Acrylic acid (1)-butyl acrylate (2)				
19.3	16.5	0.58	1.07	2.73	0.35
38.6	33.9				
57.9	52.4				
77.2	67.9				
	Acrylic acid (1)-butyl methacrylate (2)				
19.8	6.3	0.29	3.67	0.73	0.50
39.6	15.5				
59.4	30.5				
79.2	47.8				
	Methacrylic acid (1)-butyl acrylate (2)				
20	35.3	1.31	0.35	5.82	0.15
40	57.6				
60	70.1				
80	84.6				
	Methacrylic acid (1)-butyl methacrylate (2)				
22.1	18.7	0.75	1.20	1.84	0.25
43.1	37.2				
63.0	56.4				
81.9	78.9				

TABLE II

Copolymerization Parameters, Q and e, from Literature (1)

Monomer	Q	e
Acrylic acid	1.15	0.77
Butyl acrylate	0.51	1.02
Methacrylic acid	2.34	.65
Butyl methacrylate	0.72	−.23

TABLE III

Correction of Acrylate-Methacrylate Data for Acid Lag

Monomer		Polymer		
% methacrylate	% acid	Δ acid	% methacrylate	Corrected % methacrylate
BuA-MAA			(BuMA-MAA)	
20	20	−3.0	35.3	38.3
40	40	−5.5	57.6	63.1
60	60	−6.0	70.1	76.1
80	80	−6.5	84.6	91.1
BuMA-AA			(BuA-AA)	
20.8	79.2	−4.5	52.2	47.7
40.6	59.4	−6.5	69.5	63.0
60.4	39.6	−5.5	84.5	79.0
80.2	19.8	−3.0	93.7	90.7

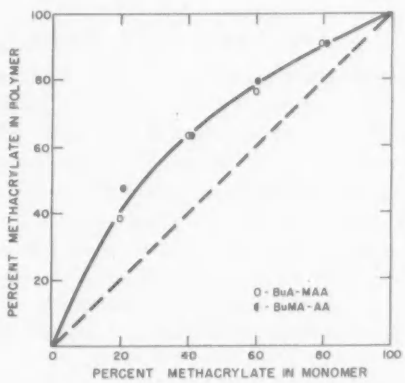

Fig. 2. Copolymerization of acrylate with methacrylate corrected for acid retardation.

ratios, r_1 and r_2, and also the reactivity ratios calculated from the Q and e values of Young (1) shown in Table II. The composition curves which may be calculated from the latter reactivity ratios are quite unlike the experimental ones, and in some cases they deviate from the ideal in the opposite direction. It is regrettable that the Q and e parameters should prove to be so unreliable.

The copolymerizations of acid monomers with the corresponding butyl esters are very nearly ideal; the entry of acid into the copolymer is slightly retarded in both cases by about the same amount. This may be due to ionic repulsion in the polar solvent ethanol, or to a lowering of the effective monomer concentration due to ionization. In any event the retardation is in qualitative agreement with the results of Alfrey, Overberger, and Pinner (2) who found that the ionized form of methacrylic acid was much less reactive than the un-ionized form.

We have polymerized an acrylic monomer with a methacrylic monomer in two cases, MAA-BuA and AA-BuMA. These are diverted from ideal behavior by two factors: the acrylate-methacrylate effect and the acid-butyl ester effect. We can correct these two composition curves for the acid effect as follows: add to the per cent methacrylate for the MAA-BuA curve the amount the MAA-BuMA curve falls below ideal, and subtract from the per cent methacrylate for the AA-BuMA curve the amount the AA-BuA curve falls below ideal. The results are shown in Figure 2 and Table III, where it is seen that the two series agree very well in describing the copolymerization of acrylate and methacrylate. Taking methacrylate as monomer 1, the reactivity ratios are $r_1 = 2.2$ and $r_2 = 0.3$.

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POLYMER LETTERS VOL. 1, PP. 77-78 (1963)

ON A RELATIONSHIP BETWEEN STEREOREGULARITY AND PARTICLE SIZE BROADENING*

In their classic work on the distribution of crystallite sizes, Warren and Averbach (1) showed that the integral breadth, β, of a diffraction profile is given by

$$\beta = \lambda/a \cos\theta \sum_{-\infty}^{\infty} A_n \tag{1}$$

where λ is the wavelength of the incident radiation, θ is the diffracting angle for the given reflection, and a is the crystallographic spacing for the reflection. The coefficients, A_n, are given by

$$A_n = (1/N) \sum_{|n|+1}^{\infty} (i - |n|)n_i \tag{2}$$

where n_i is the number of "columns of length i cells," i.e., the distribution function for the column lengths, and N is the total number of cells in the sample.

Let us consider crystallization of a stereoregular polymer with the distribution of tactic sequences (2) given by

$$\begin{aligned} N_I(m) &= P_{d11}P_{11d}P_{111}^{m-2} \qquad m > 1 \\ N_I(1) &= P_{d1d} \end{aligned} \tag{3}$$

where P_{ijk} is the probability of adding a monomer unit in configuration k to a growing chain ending in i–j. If we now assume that under equilibrium conditions all tactic sequences of length m form crystallites of length m (most appropriate to annealed fibers), we may relate the integral breadths of reflections along the chain axis to the stereoregularity of a sample. We will first assert that a critical crystallite length, m_0, exists such that only those chains which have a sequence length greater than this may crystallize (3). We may then identify n_i of eq. (2) with N_I as restricted by the above assumptions. It may then be shown that substitution of N_I into eq. (2), followed by insertion of the result into eq. (1), leads to

*No. 6 in a series on stereoregularity. Contribution No. 141 from Chemstrand Research Center, Inc.

$$1/\beta \propto \sum_{n=-\infty}^{\infty} A_n = [P_{111} + (1 + m_0 P_{11d})^2]/[P_{11d}(1 + m_0 P_{11d})] \qquad (4)$$

with $P_{111} = 1 - P_{11d}$.

We recognize the right-hand side of this equation as the "weight-average sequence length," $\left\langle L_{wI}^{m_0} \right\rangle$, for sequences longer than m_0, and thus

$$\beta \propto 1/\left\langle L_{wI}^{m_0} \right\rangle \qquad (5)$$

Although this result is not surprising it is significant in that it demonstrates that the weight-average, rather than the number-average, crystallite length determines the integral breadth. Equation (5) was developed for an isotactic polymer; an analogous form is obtained for a syndiotactic polymer.

From eq. (4) it is seen that the integral breadth of the diffraction peak is determined by the single addition probability P_{11d} and by the minimum crystallite size m_0 (a constant for a given polymer). Since P_{11d} may be determined directly from the melting point (4), we have the surprising result that the integral breadth of a diffraction peak may be determined only by the equilibrium melting point, and is not otherwise influenced by stereoregularity. Thus, in those cases in which melting point measurements may not be made directly, a qualitative estimate of melting points may be made from measurements of diffraction profiles.

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POLYMER LETTERS VOL. 1, PP. 79-81 (1963)

KINETICS OF STEREOSPECIFIC POLYMERIZATION OF 1,3-BUTADIENE

Kinetics studies on the polymerization of 1,3-butadiene with aluminum triisobutyl-titanium tetrachloride catalyst have been reported (1).

It is known that with such a catalyst it is possible to obtain polymers mainly 1,4-trans or amorphous polymers consisting of a mixture of macromolecules having a 1,4-cis and 1,4-trans structure, depending on the Al/Ti ratio (2).

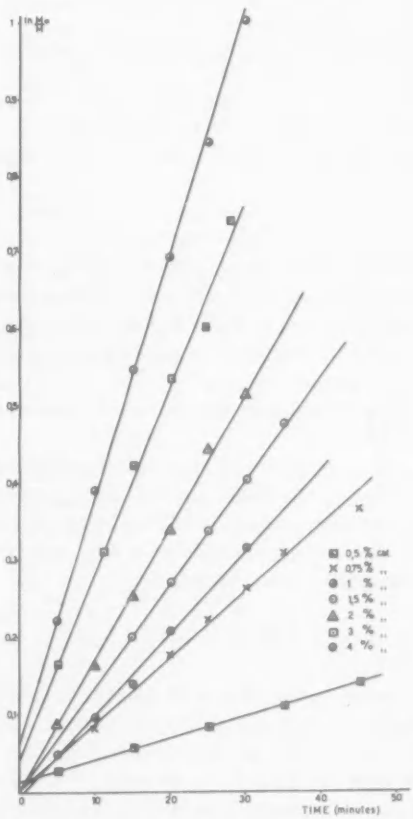

Fig. 1. Plot of butadiene polymerization rate for different catalyst concentrations. Butadiene, 30 g. Toluene, 400 ml. T, 0°C.

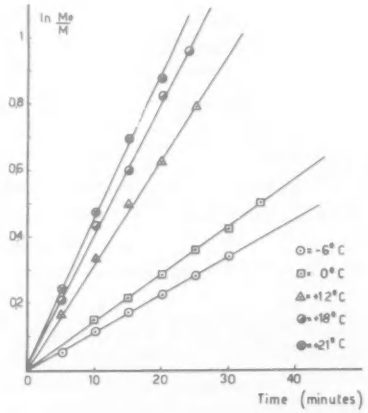

Fig. 2. Influence of temperature on the polymerization rate. Butadiene, 30 g. Toluene, 400 ml. Total catalyst, 1.5 g. for 100 g. of monomer.

We were successful in obtaining a polymer consisting of macromolecules having mainly the 1,4-cis structure (up to 96%) by means of a three-component catalytic system not containing metal-alkyls (3).

Using the aforesaid catalytic system, we carried out several polymerization in toluene solution in order to investigate the kinetics of the reaction. The data were obtained by analyzing for solids in samples collected at different times from a cylindrical vessel equipped with a stirrer and maintained at constant temperature by means of a thermostatic system.

When the catalyst is prepared in the presence of monomer and in dilute solution, the reaction takes place in homogeneous phase.

By plotting ln(Mo/M) versus time (Fig. 1) we obtained straight lines, which indicate that the rate is first order with respect to monomer; therefore, in the general rate equation:

$$- dM/dt = K[M]^{\alpha} \cdot [Cat]^{\beta}$$

$\alpha = 1$. A first-order dependence with respect to catalyst is also obtained calculating ln(Mo/M)/t and plotting it against different initial catalyst concentrations; a straight line is obtained, thus showing that $\beta = 1$.

The results agree with those found earlier (1), although in that instance catalysis is heterogeneous and reaction is carried out at molar ratio Al/Ti = 1. The resulting product has the 1,4-trans structure, in comparison with the 1,4-cis structure of our product.

Molar ratios of the components of the presently considered catalyst do not influence the structure of the resulting polymer. These ratios are within the range where the maximum reaction rate is observed.

Figure 2 shows the influence of temperature on the rate constant in experiments performed at constant monomer and catalyst concentrations. An usual plot of log K versus 1/T gives activation energy value about 9 kcal./mole.

However, when the catalyst is prepared in the absence of monomer, generally the dependence on the catalyst concentration is not simple ($\beta \neq 1$), and the polymerization rate is slower.

More detailed data on the peculiarities of the catalytic system and on the experimental technique will appear soon.

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POLYMER LETTERS VOL. 1, PP. 83-86 (1963)

AVOIDING THE USE OF THE TIME DERIVATIVE IN REACTION RATE STUDIES: A SIMPLIFIED DERIVATION OF TOBOLSKY'S DEAD END RADICAL POLYMERIZATION EQUATION

It is suggested that since so many new and improved analytical tools are now at our disposal, mechanism studies may be made by comparing disappearances of components (or appearances of product) with respect to each other as well as with respect to time. This procedure often simplifies a cumbersome relationship (1) and invariably hypothesises a necessary condition for the mechanism under consideration. A few applications of this principle will be presented.

1. Tobolsky (2) developed an equation which states that for radical initiated vinyl polymerization in the absence of both thermal polymerization and the Tromsdorf-Norrish (3) effect, if the initator disappears by a first-order process, there is a limiting monomer conversion. Starting with

$$-d[M]/dt = K[M][Cat]^{1/2} \tag{1}$$

$$-d[Cat]/dt = k[Cat] \tag{2}$$

Instead of finding the solution to these two equations separately as Tobolsky does, we divide eq. (1) by eq. (2)

$$d[M]/d[Cat] = K[M]/k[Cat]^{1/2}$$

$$\int_{[Mo]}^{[M]} d[M]/[M] = \int_{[Cat_0]}^{[Cat]} Kd[Cat]/k[Cat]^{1/2}$$

$$\ln([M]/[Mo]) = 2K([Cat]^{1/2} - [Cat_0]^{1/2})/k$$

$$\lim_{[Cat]\to 0} \{\ln([M]/[Mo])\} = -2[Cat_0]^{1/2}/k \tag{3}$$

Equation (3) is identical to Tobolsky's.

2. An initiator which disappears by a second order process would give the following result:

$$-d[M]/dt = K[M][Cat]$$

$$-d[Cat]/dt = k[Cat]^2$$

$$d[M]/d[Cat] = K[M]/k[Cat]$$

$$\int_{[M_0]}^{[M]} d[M]/[M] = \int_{[Cat_0]}^{[Cat]} Kd[Cat]/k[Cat]$$

$$\ln ([M]/[Mo]) = (K/k) \ln ([Cat]/[Cat_0]) \qquad (4)$$

$$\lim_{[Cat]\to 0} [M] = 0$$

The result implies that a bimolecular initiation can give no limiting conversion.

O'Driscoll and McArdle (4) extended Tobolsky's original relationship to include bimolecular initiation, such that the two species were different. The derivation is appropriate for the initiating system benzoyl peroxide-dimethyl aniline.

$$-d[M]/dt = K[M][ab]^{1/2}$$

$$-d[a]/dt = -d[b]/dt = k[ab]$$

$$d[a]/d[b] = 1 \qquad (5)$$

$$[a] = [a_0] - [b_0] + [b]$$

$$d[M]/d[b] = K[M][ab]^{-1/2}/k$$

$$\int_{[M_0]}^{[M]} d[M]/[M] = \int_{[b_0]}^{[b]} (K/k) \{[b]([a_0] - [b_0] + [b])\}^{-1/2} d[b]$$

$$\ln ([M]/[Mo]) = (K/k) \ln \left\{ \frac{2([b]^2[a_0]\,[b] - [b_0][b])^{1/2} + 2[b] + [a_0] - [b_0]}{([b_0]^{1/2} + [a_0]^{1/2})^2} \right\}$$

$$\lim_{[b]\to 0} \{\ln ([M]/[Mo])\} = (K/k) \ln \{([a_0] - [b_0])/([a_0]^{1/2} + [b_0]^{1/2})\} \qquad (6)$$

It is clear that for $[a_0] = [b_0]$, eq. (6) and eq. (4) are identical and equal molar mixtures of benzoyl peroxide and dimethyl aniline should give no limiting conversion providing eq. (5) holds.

4. Dewar (5) cites a general kinetic scheme which frequently occurs. A + B + C ⟶ products, which takes place by the reversible formation of an intermediate X from A and B followed by reaction of C with X.

$$A + B \xrightarrow{1} X$$

$$X \xrightarrow{2} A + B$$

$$C + X \xrightarrow{3} \text{products}$$

$$-d[A]/dt = -d[B]/dt = k_1[A][B] - k_2[X]$$

$$-d[C]/dt = k_3[C][X]$$

$$d[X]/dt = 0 = k_1[A][B] - k_2[X] - k_3[C][X]$$

$$[X] = k_1[A][B]/(k_2 + k_3[C])$$

$$-d[A]/dt = -d[B]/dt = k_1[A][B]\{1 - k_2/(k_2 + k_3[C])\} \quad (7)$$

$$-d[C]/dt = k_1k_3[A][B][C]/(k_2 + k_3[C]) \quad (8)$$

$$d[A]/d[B] = d[A]/d[C] = d[B]/d[C] = 1 \quad (9)$$

The simplicity of eqs. (9) compared to eqs. (7) and (8) is extreme, yet eqs. (9) is just as necessary a condition for the mechanism as eqs. (7) and (8).

5. For the case of a two component system $2A + B \longrightarrow$ products through an intermediate X which reacts with A:

$$A + B \xrightarrow{1} X$$

$$X \xrightarrow{2} A + B$$

$$A + X \xrightarrow{3} \text{products}$$

$$-d[A]/dt = k_1[A][B]\{1 - k_2/(k_2 + k_3[A]) + k_3[A]/(k_2 + k_3[A])\}$$

$$-d[B]/dt = k_1[A][B]\{1 - k_2/(k_2 + k_3[A])\}$$

$$d[A]/d[B] = 2$$

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A NOTE ON CRANK'S CORRESPONDENCE PRINCIPLE IN DIFFUSION WITH A VARIABLE DIFFUSION COEFFICIENT

Solutions of the diffusion equation with a variable diffusion coefficient can, as a rule, be obtained only by lengthy procedures. Therefore, it seems worthwhile to point to a general correspondence principle, briefly mentioned by Crank (1), according to which each such solution describes in fact not only one, but two different diffusion problems with different dependence of the diffusion coefficient on concentration. Although Crank restricts his brief remark to uni-dimensional sorption and desorption under simple initial and boundary conditions, his correspondence principle is actually much more general.

A simple example will be considered first. The diffusion equation for one species, i, in one dimension and in the absence of convection, sources and sinks, and thermal diffusion may be written as

$$\partial C_i/\partial t = \text{div } (D_i \text{ grad } C_i) \tag{1}$$

where the diffusion coefficient will first be assumed to depend on concentration only:

$$D_i = f_1(C_i) \tag{2}$$

where f_1 is any known function of concentration. Suppose that the initial and boundary conditions are

$$t = 0, \quad x > 0, \qquad C_i = f_2(x) \tag{3}$$

$$t \geq 0, \quad x = 0, \qquad C_i = f_3(t) \tag{4}$$

where f_2 and f_3 are known functions of the space coordinate and time, respectively. The solution, in general terms, may be written as

$$C_i = F(x,t) \tag{5}$$

giving the concentration as a function of space and time.

It is easy to verify that the solution of the problem remains the same if C_i is replaced throughout by $C^0 - C_j$, where C_j is variable and C^0 is a constant equal to or greater than the maximum concentration C_i occurring in the problem. Accordingly, the solution $F(x,t)$, once calculated, can also be used to obtain, in a simple manner, the solution of the following different problem:

TABLE I

Concentration Dependences of Diffusion Coefficients Corresponding to One Another in Sorption and Desorption

Concentration dependence of diffusion coefficient		Interrelation of limiting diffusion coefficients	Limits for parameters
Sorption	Desorption		
$f_1(C) = f_1(0)$	$g_1(C) = g_1(0)$	$g_1(0) = f_1(0)$	
$= f_1(0)\left[1 + a\frac{C}{C^0}\right]$	$= g_1(0)\left[1 - \frac{a}{a+1}\frac{C}{C^0}\right]$	$= f_1(0)\ [1 + a]$	$-1 < a < \infty$
$= f_1(0)\left[1 + a\sqrt{\frac{C}{C^0}}\right]$	$= g_1(0)\left[1 - \frac{a}{a+1}\sqrt{\frac{C}{C^0}}\right]$	$= f_1(0)\ [1 + a]$	$-1 < a < \infty$

$= f_1(0)\ \dfrac{1}{1 - a\dfrac{C}{C^0}}$	$= g_1(0)\ \dfrac{1}{1 - \dfrac{a}{a-1}\dfrac{C}{C^0}}$	$= f_1(0)\ \dfrac{1}{1-a}$	$-\infty < a < 1$
$= f_1(0)\ \dfrac{1}{\left(1 - a\dfrac{C}{C^0}\right)^2}$	$= g_1(0)\ \dfrac{1}{\left(1 - \dfrac{a}{a-1}\dfrac{C}{C^0}\right)^2}$	$= f_1(0)\ \dfrac{1}{(1-a)^2}$	$-\infty < a < 1$
$= f_1(0)\ \dfrac{1 - b\dfrac{C}{C^0}}{1 - a\dfrac{C}{C^0}}$	$= g_1(0)\ \dfrac{1 - \dfrac{b}{b-1}\dfrac{C}{C^0}}{1 - \dfrac{a}{a-1}\dfrac{C}{C^0}}$	$= f_1(0)\ \dfrac{1-b}{1-a}$	$-\infty < a < 1$ $-\infty < b < 1$
$= f_1(0)\ \exp\left\{a\dfrac{C}{C^0}\right\}$	$= g_1(0)\ \exp\left\{-a\dfrac{C}{C^0}\right\}$	$= f_1(0)\ \exp\{a\}$	None

$$\partial C_j/\partial t = \text{div } (D_j \text{ grad } C_j) \tag{1a}$$

$$D_j = g_1(C_j) = f_1(C^0 - C_j) \tag{2a}$$

$$t = 0, \quad x > 0, \qquad C_j = g_2(x) = C^0 - f_2(x) \tag{3a}$$

$$t \geq 0, \quad x = 0, \qquad C_j = g_3(t) = C^0 - f_3(t) \tag{4a}$$

the solution G(x,t) being

$$C_j = G(x,t) = C^0 - F(x,t) \tag{5a}$$

Here, g_1, g_2, and g_3 are functions related to f_1, f_2, and f_3 as indicated.

As an illustration, Table I lists various typical concentration dependences f_1 and g_1 of diffusion coefficients corresponding to one another in sorption and desorption. In Table I, $f_1(0)$ and $g_1(0)$ are the diffusion coefficients at zero concentration of the species, and the constant parameters a and b are the same for corresponding cases. The headings, sorption and desorption, can, of course, be interchanged.

It is evident from the form of eq. (1) that the correspondence principle also applies to diffusion in two and three dimensions. Furthermore, the diffusion coefficient may also depend on time, location, and absolute value of the concentration gradient, provided that these dependences are the same in corresponding functions f_1 and g_1. The diffusion coefficient may also depend on temperature and on stress exerted by the medium, provided that the profiles of both temperature and stress are the same in both corresponding cases. Last, but not least, the correspondence principle also holds for anisotropic media, provided that each of the diffusion coefficients along the principal axes obey a correspondence relation of the type of eq. (2a).

A physical interpretation of the correspondence principle is readily given and may serve to explain the basis and generality without recourse to mathematics. Any redistribution of one species i by diffusion can be considered formally as a simultaneous redistribution of <u>two</u> species i and j, where the fictitious second species j is complementary to i so that, at any location and time, the sum of the concentrations of both species is constant:

$$C_i(x,t) + C_j(x,t) = C^0 = \text{const.} \tag{6}$$

For example, species j can be thought of as the "void" that can be occupied by i, and C^0 would then correspond to a maximum "capacity". [The second species may be real rather than fictitious. Examples are binary interdiffusion of counterions in ion exchangers where eq. (6) (with concentrations given in equivalents) is the electroneutrality condi-

tion, and binary interdiffusion with a constant-volume restriction (with concentrations given as volume fractions).] With the condition (6) the flux of j is automatically equal in magnitude (and opposite in sign) to that of i, and the same is true for the concentration gradients. If both species are to obey the diffusion equation (1), their diffusion coefficients D_i and D_j must be identical at any location and time (C_i and C_j, of course, being normally different). From $D_i = D_j$ and condition (6) one obtains at once the interrelation of the concentration dependences $f_1(C_i)$ and $g_1(C_j)$ as given in eq. (2a). Essentially the same argument applies to more complex systems, as discussed before.

Symbols

C = concentration.
D = diffusion coefficient.
x = space coordinate.
t = time.
Indices i and j refer to the respective diffusing species.

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THE INFLUENCE OF MOLECULAR WEIGHT DISTRIBUTION ON THE SOLUBILITY ANALYSIS OF IRRADIATED RUBBER

The techniques commonly used to estimate crosslinking in polymers may be misleading when applied in radiation studies because of the occurrence of chain fracture. Charlesby and Pinner (1) have presented an analysis which takes into account both crosslinking and fracture of a polymer with a random molecular weight distribution. A polymer with an average of u units per molecule gives a sol fraction (s) after a radiation dose of R which may be related to the probabilities that a unit is fractured (p) or crosslinked (q) per unit dose (eq. 1).

$$s + s^{1/2} = pq^{-1} + (quR)^{-1} \qquad (1)$$

The molecular weight distribution of a polymer is not usually random but eq. (1) has been applied with considerable success in cases where extensive radiation-induced fracture has eventually randomized the initial distribution. Successful application of the equation has also been reported for natural rubber (2) but in these laboratories we observe nonlinear plots of $s + s^{1/2}$ vs. R^{-1} as exemplified in Figure 1 for a purified sample (sol fraction of acetone extracted crepe). We attributed this discrepancy with eq. (1) to a nonrandom distribution in the rubber and a relatively low incidence of radiation-induced fracture (3).

We have sought to get agreement with eq. (1) by working with a sample of rubber possessing a nearly random molecular weight distribution. This objective was facilitated by the work of a colleague, Mr. C. L. Bell, who has found that the randomization of molecular weight of rubber in solution can be achieved by thermal oxidation initiated by decomposi-

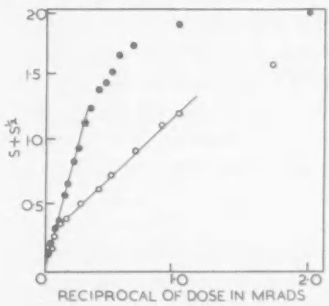

Fig. 1. Solubility of samples irradiated at 1 Mrad/min. at 25°C. (o) Nonrandomized sample (M_n, number-average molecular weight, = 4.8×10^5); (●) partially randomized sample ($M_n = 1.5 \times 10^5$).

tion of azobisisobutyronitrile. After such treatment followed by the destruction of residual peroxide groups, the rubber was recovered from solution. Partial randomization is evidenced by a decrease in the ratio of weight to number-average molecular weights from 3.1 in the initial sample to 2.5, i.e., towards the theoretical ratio of 2 for a random distribution.

The results obtained when the initial and partially randomized samples were exposed in vacuo to 4 mev electrons from a linear accelerator are shown in Figure 1. Apparently, as a result of partial randomization agreement with eq. (1) is obtained at higher doses. Evidence that the observed slope gives a reasonable estimate of G(X, crosslinks) is provided by good agreement with the results of other methods (Table I).

TABLE I

Estimates of Crosslinks and Fractures

Method	Swelling (4)	Elastic measurements (5)	Solubility analysis
G(X)	0.7_5	1.0_5	0.85^2 0.9
pq^{-1}	Assumed = 0	0.11	0.05^2 0.05

The estimate of the ratio of fractures to crosslinks from the intercept in Figure 1, pq^{-1}, is lower than one derived from elastic measurements. However, the internal consistence of the solubility method has been demonstrated by showing that a similar limiting value of pq^{-1}, 0.04 – 0.07, is obtained by re-irradiation of a rubber network from which all soluble matter had been extracted.

A reasonable G(X) value of 1.0 may also be derived from the slope obtained from the nonrandomized sample of rubber as defined by values of $s + s^{1/2}$ in the range from about 0.4 to 1.2. However, extrapolation of this line to the $s + s^{1/2}$ axis would give a gross overestimate of pq^{-1} which is, instead, defined by the approach to limiting solubility at high doses. These results would seem explicable if "ordinary" samples of rubber approximate to a random distribution but with superimposed tails of high and low molecular weight. The presence of such tails is suggested by fractionation data (6).

This work was completed in the laboratories of the Natural Rubber Producers' Research Association. Samples were irradiated at Wantage Research Laboratories (Atomic Energy Research Establishment) with the kind cooperation of Dr. R. Roberts and Mr. J. McCann.

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THE ROLE OF AN ADDITIVE IN REDUCING NETWORK FORMATION ON IRRADIATION OF RUBBER

Values for G(X) and $G(H_2)$ of 0.9 and 0.65, respectively, are consistent with eq. (1) which illustrates the predominant reaction responsible for network formation on irradiation of rubber (RH) (1,2). It has been

$$2RH \rightsquigarrow R{-}R + H_2 \qquad (1)$$

shown that free radical scavengers greatly retard network formation at concentrations at which they have a relatively small effect on the yield of hydrogen (2,3). For example, 2.5×10^{-4} moles of nitrobenzene was estimated to suppress 70% of the physical crosslinks (carbon-carbon crosslinks plus "entanglements") and to reduce the yield of hydrogen by about 10%. This was interpreted to mean that eq. (1) could be largely resolved into the free radical reactions (2) to (4), the role of the scavenger being to intercept rubber radicals (R·) which would otherwise combine to yield crosslinks

$$RH \rightsquigarrow R\cdot + H\cdot \qquad (2)$$

$$H\cdot + RH \longrightarrow R\cdot + H_2 \qquad (3)$$

$$2R\cdot \longrightarrow R{-}R \qquad (4)$$

The above estimate of crosslinks was derived from swelling data on the assumption that chain fracture is not affected by the additive. Recent stress-relaxation studies of irradiated rubber networks containing additives (4) suggest that this assumption is invalid, but the data obtained are not amenable to quantitative analysis (5). The purpose of this note is to report unambiguous data obtained by solubility analysis on the role

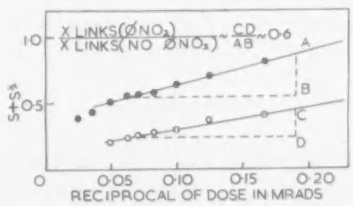

Fig. 1. Solubility of rubber irradiated in electron beam from linear accelerator at 1 Mrad/min. (○) Rubber; (●) rubber plus nitrobenzene.

of an additive in reducing network formation on irradiation of rubber.

A sample of high molecular weight rubber (sol fraction of acetone-extracted crepe) was used in order to study gelation in the presence of a network retarder after reasonably low doses. Nitrobenzene, which is miscible with rubber, was added with a micrometer syringe and homogeneous samples exposed in vacuo to 4 mev electrons at 25°C. After irradiation the additive was removed with acetone prior to extraction of the samples with a rubber solvent.

Comparison of the approximately linear slopes obtained by plotting $S + S^{\frac{1}{2}}$ vs. R^{-1} in Figure 1 shows that the additive suppresses about 40% of the carbon-carbon crosslinks (cf. ref. 1). The high value of 70% previously estimated from swelling data may be attributed to erroneous inclusion of a process of network destruction due to increased chain fracture in the presence of the additive. Experiments on the limiting solubility developed on irradiation of networks initially free of soluble rubber showed that nitrobenzene increased the ratio of fractures to crosslinks from the usual value of 0.05 to 0.16. The influence of the additive is summarized in Table I by reference to a G(X) value for pure rubber of 0.9.

TABLE I

Influence of Nitrobenzene on Crosslinking and Fracture.

	No additive	Nitrobenzene (2.5×10^{-4} m./g.)
G(X)	0.9	0.5_5
G(F)	0.04_5	0.08_5

The present data indicate that eq. (1) is to be regarded as an important "molecular" crosslinking reaction on irradiation of rubber but that radical reactions such as (2)-(4) also occur.

This work was completed in the laboratories of the Natural Rubber Producers' Research Association. Samples were irradiated at Wantage Research Laboratories (Atomic Energy Research Establishment) with the kind cooperation of Dr. R. Roberts and Mr. J. McCann.

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THE INFLUENCE OF THE TEMPERATURE OF IRRADIATION ON THE FORMATION OF POLYMER NETWORKS

Network formation on irradiation of a hydrocarbon polymer (RH) is generally attributed to crosslinking associated with hydrogen formation (eq. 1). A serious objection made to this mechanism is based on the assertion that on lowering the temperature of irradiation the yield of hydrogen remains constant and yet the yield of crosslinks decreases.

(1)

In the case of rubber it has been reported that the yield of crosslinks is reduced to about one-quarter by lowering the temperature of irradiation from 25 to −196°C. (1). This conclusion was based on the analysis of solubility data, but as complex results may be obtained with ordinary rubber, the work was repeated with samples which had been partially randomized (2). The results shown in Figure 1 do not agree with the previous conclusions but instead indicate that the yield of crosslinks, like the yield of hydrogen (3), is largely independent of temperature. The observation that at −196°C. the yield of fractures is increased, pq^{-1} increasing threefold, accounts for an accompanying increase in equilibrium swelling values reported in earlier work (3).

Doubts concerning the applicability of eq. (1) have been expressed most lucidly in the case of polyethylene (4). Although extensive data

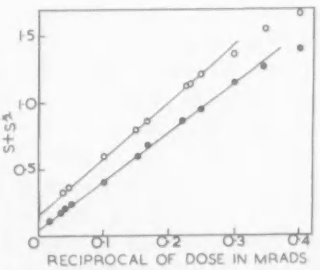

Fig. 1. Solubility of rubber irradiated in 4 mev electron beam from linear accelerator at 1 Mrad/min. (○) −196°C.; (●) 25°C. G(X, −196°) = 0.9G(X, 25°).

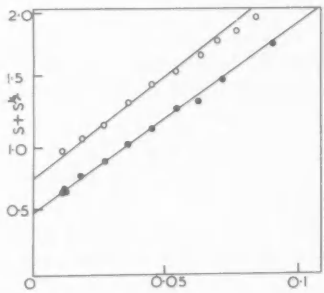

Fig. 2. Solubility of polyethylene irradiated in 4 mev electron beam at 1 Mrad/min. (○) −196°C.; (●) 25°C. Abscissa: Reciprocal of dose in Mrads. G(X, −196°) = (0.9–1.1)G(X, 25°).

have been reported on network formation in this polymer at −196°C., it is ambiguous in the sense that it does not distinguish between crosslinking and fracture. Therefore, a sample of high density polyethylene (Marlex 50) was irradiated in vacuo at 25 and −196°C. One day after irradiation all the samples together were repeatedly melted at 140°C., while still in vacuo, to remove trapped radicals. The samples were then sealed in a tube with carefully degassed xylene, containing an antioxidant (di-sec-octyl-p-phenylenediamine) and kept for three days at 110°C. The solvent was replaced and the extraction repeated under similar conditions. This care to avoid post-irradiation oxidative degradation is detailed because the ratio of fractures to crosslinks at 25°C, $pq^{-1} \sim 0{\cdot}45$, is higher than previously reported values which range between 0.2-0.3. Notwithstanding this discrepancy, the results in Figure 2 reveal that on lowering the temperature of irradiation the yield of crosslinks is scarcely affected and also strongly suggest that the yield of fractures is increased.

The present results with both rubber and polyethylene restore confidence in the hydrogen-crosslinking mechanism and make it unnecessary to invoke alternative modes of network formation such as "endlinking" (5). However, they raise the new problem of why the yield of fractures should be increased at low temperatures.

This work was completed in the laboratories of the Natural Rubber Producers' Research Association. Samples were irradiated at Wantage Research Laboratories (Atomic Energy Research Establishment) with the kind cooperation of Dr. R. Roberts and Mr. J. McCann.

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ISOLATION OF A CYCLIC TRIMER FROM POLY (1,4-CYCLOHEXYLENEDIMETHYLENE TEREPHTHALATE)

During our investigations on oligoesters we extracted granular poly (1,4-cyclohexylenedimethylene terephthalate) (Eastman Kodak Co.) with dioxane for about 160 hr. Removal of the solvent from the extract gave approximately 0.4% of a solid, from which by treatment with methanol and fractional crystallization from benzene and benzene/light petroleum several fractions have been obtained:

A: m.p. 225-245°C., from the cooled dioxane solution.
B: m.p. 118-125°C., soluble in hot methanol, recrystallized from benzene/light petroleum.
C: m.p. 195-215°C., from benzene.
D: m.p. 160-164°C., from benzene/light petroleum.
E: m.p. 288-298°C., from benzene/light petroleum.

Fraction E formed the main amount of the extracted material and has been examined in more detail. It crystallized from benzene/light petroleum in long rods or needles. It showed the same elementary analysis as the polymer and a molecular weight as a trimer:

$(C_{16}H_{18}O_4)_x$	Calculated:	C, 69.9%; H, 6.62%
	Found:	C, 69.8%; H, 6.57%

Molecular weight:

$(C_{16}H_{18}O_4)_3$	Calculated:	823
	Found:	(a) cryoscopically 870, 821, 868.
		(b) In the vapor pressure osmometer 803.

In connection with IR- and x-ray examination, these results can be reconciled only with a cyclic structure. A linear trimer oligoester would have another elementary analysis. Its infrared absorption spectrum would show characteristic absorptions for the terminal groups and the x-ray powder diagram would be more similar to that of the polymer. In addition, a linear oligoester with a molecular weight of 800 would not be macrocrystalline. The cyclic trimer melted over a range of 10°. This may be caused by decomposition at 280°C. or by an isomerization of the 1,4-cyclohexane-dimethanol.

We are about to investigate the characterization of the rest of the polymer extract and the synthesis of oligoesters as model compounds.

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COPOLYMERIZATION OF VINYL ACETATE AND SULFUR DIOXIDE BY IONIZING RADIATION

Earlier studies has been made on the copolymerizations of sulfur dioxide with polymeric monomers, especially with olefins (1-4), which result in the formation of polysulfones. They were carried out in the liquid state by catalyst, light, or ionizing radiation (3) and had a distinct ceiling temperature (1).

The present report deals with the copolymerization of mixtures of equal moles of vinyl acetate and sulfur dioxide by gamma rays from a kilo-curie of Co^{60}, and finds that the ceiling temperature is situated at about $-20°C$. and that solid state polymerization occurs in the vicinity of $-150°C$.

Vinyl acetate monomer was evacuated at 10^{-3} mm. Hg, distilled into 15 ml. ampules into which sulfur dioxide was introduced from a gas reservoir by means of a liquid nitrogen bath, and then the ampules were sealed at the neck by a flame. The samples obtained were then irradi-

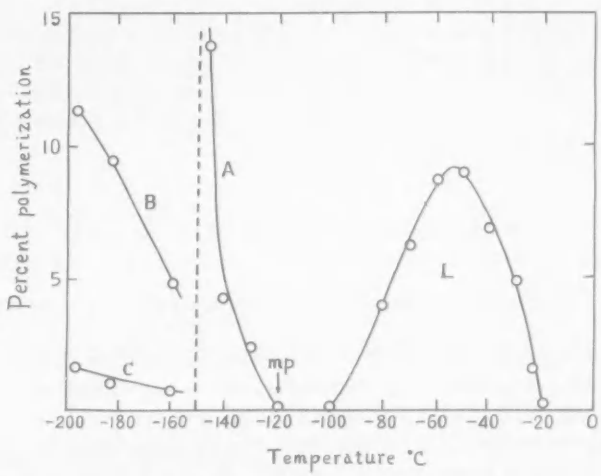

Fig. 1. Copolymerization of vinyl acetate and sulfur dioxide at different temperatures. Dose rate is 7.2×10 r/hr. at 3.5 hr. duration. Irradiation was carried out in liquid state (L); in solid state (A); post-treated at $-140°C$. (B); post-treated at $20°C$. or in the presence of 0.7% DPPH (C). The dotted line indicates the probable maximum point of polymerization.

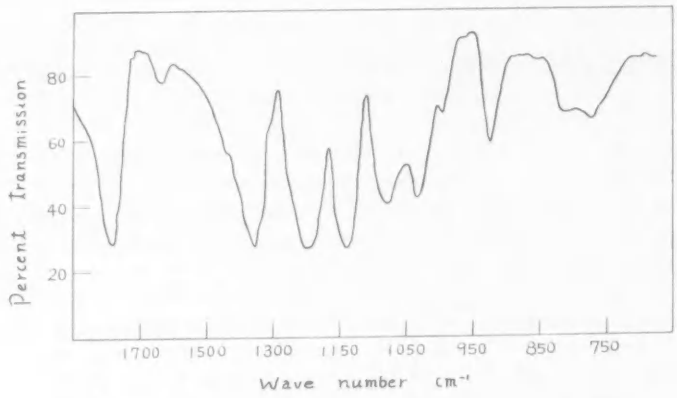

Fig. 2a. Infrared absorption spectrum of the copolymer.

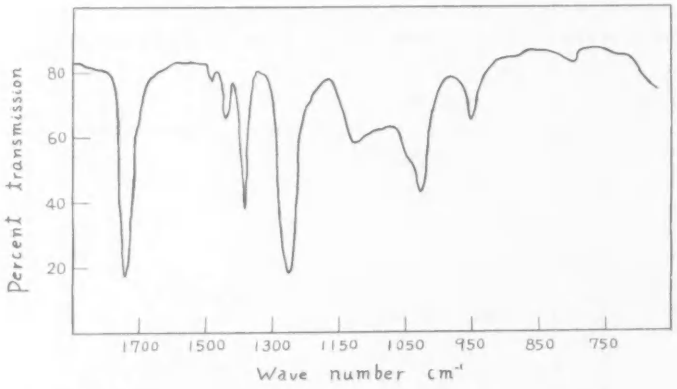

Fig. 2b. Infrared absorption spectrum of poly(vinyl acetate).

ated in the range of room to liquid nitrogen temperature. To determine the yields of polymer, the irradiated samples were opened at various temperatures, methanol was added, and the polymer residues weighed.

Polymerization yield vs. temperature in the liquid state is shown in Figure 1(L) at a dose rate of 7.2×10^4 r/hr. and a duration of 3.5 hr. The ceiling temperature is located at about $-20°C.$, the polymerization maximum is near $-60°C.$, and polymerization does not occur from $-100°C.$ down to the $-120°C.$ melting point of the starting mixture.

Infrared absorption spectra of the polymers by means of the KBr disk method are indicated in Figures 2a,and 2b which is of pure poly(vinyl

acetate). It is seen in Figure 2a that the polymer obtained has the $-SO_2-$ group located at 1350 and 1140 cm.$^{-1}$, C-S-C at 775 cm.$^{-1}$, and C-S stretching at 645 and 590 cm.$^{-1}$ which is not shown here but is in the KBr region. Location of the ester group at 1770 and 1190 cm.$^{-1}$ is slightly transfered from the corresponding one of pure poly(vinyl acetate).

Micro-analytical determination of sulfur yields a value of 20-21%, which shows that this polymer has a 1:1 composition.

When irradiation is carried out below the melting point of the mixture (−120°C.), the results shown in Figure (A, B, C) are obtained.

In the experiment shown by curve A, a methanol solution of DPPH was poured into the sample tube after irradiation to prevent the after-effect by trapped radicals. The results suggest that copolymerization has occurred in the range −120 and −150°C.

In the experiment shown by curve B, samples irradiated between −150 and −196°C. were left in a isoprene bath at −140°C. for 20 min. after irradiation and then a methanol solution of DPPH was added.

In the case of curve C, samples irradiated at the same temperature as B were plunged into a 20°C. bath, melted, and methanol was added. Moreover, irradiated samples containing 0.7% DPPH give the same curve as C, even if treated at −140°C. after irradiation in the same manner as B.

These results indicate that copolymerization occurs to a considerable extent in the solid between −120 and −150°C. but hardly occurs beneath −150°C. The higher values of B compared to C may be due to post-polymerization in solid state at −140°C.

Further details will be published later.

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LATERAL ORDER OF WET-SPUN POLYACRYLONITRILE FIBERS

The structure of polyacrylonitrile fibers has often been studied, but without obtaining conclusive results.

Kratky (1), according to an annotation of A. Prietzschk, puts forth a hexagonal unit cell with a = b = 6.17 A., and c = 5.1 A.

Point (2) proposes an arrangement of the chains of polyacrylonitrile in the form of a three-dimensional network and discusses the physical properties of PACN fibers on this basis.

Stefani, Chevreton, Garnier, and Eyraud (3) propose an ortho-rhombic base-centered unit cell with a = 10.2, b = 6.1, and c = 5.1 A. formed of syndiotactic chain segments with hydrogen bonds between nitrile groups and the hydrogens of tertiary carbon atoms. A second crystalline phase with a tetragonal unit cell a = b = 4.74, and c = 5.1 A. appears by heating stretched fibers to 120°C. The thermal treatment leads to isotactic segments of the chains; the presence of 20% of this structure in the polymer can explain the intensity of the equatorial reflection with a 3.35 A. spacing. According to Bohn, Schaefgen, and Statton (4) polyacrylonitrile exhibits only lateral order, an idea already expressed by Baker, Fuller, and Pape (5). Because of the poor longitudinal order, the authors regard the term "unit cell" for polyacrylonitrile as fallacious. The mass of this polymer is 100% laterally ordered as a single phase combining the properties of both crystalline and amorphous areas. Like Prietzschk, the authors find the lateral order of PACN to be hexagonal with 6 A. distance between the chains; but dry-spun fibers were also used in this investigation.

The question arises how wet-spun fibers behave as to their lateral order and how this is influenced by thermal treatments, plasticizer-content, and so on.

Experimental

In order to get a homopolymer of acrylonitrile, a radical solution polymerization in dimethylsulfoxide with a redox system was carried out. The polymerization was stopped at a conversion of about 60%, and the solution was passed through a thin film evaporator at 7 torr in order to remove the unreacted monomer.

The final spinning solution contained 17% polyacrylonitrile with a relative solution viscosity in dimethylformamide of $\eta_r = 1.95$ at 3 g./liter and 25°C.

For the usual wet-spinning process we used a spinneret with holes of

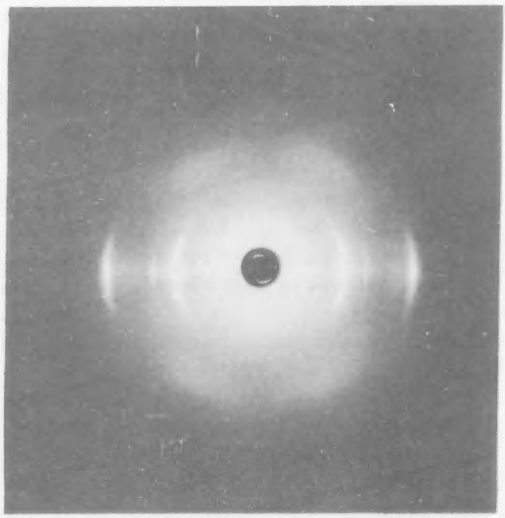

Fig. 1. X-ray diffraction pattern of our 1:15 stretched polyacrylonitrile fibers after a treatment of 30 hr. in a 30% dimethylformamide water solution and a thermosetting at 180°C. with periodical stretching and shrinking.

80μm. diameter and a 50 cm. long coagulating bath of 65% dimethylsulfoxide and 35% water. The coagulated fibers were at first prestretched to 1:5.6 in hot water and then washed. In order to dry and to increase the density and gloss of the yarn, it was passed over a row of drums heated up to 130°C. and then it was finally stretched in two stages at 170°C. to 1:15.

Monochromatic x-ray diagrams were taken of these fibers. In order to get a good resolution of the reflections, an aperture system with two circular holes of 0.6 mm. diameter, 70 mm. distant of each other, was used in our fiber camera. The distance specimen to film was 41.2 mm., found by means of a test photograph with aluminum powder on the fibers, especially from the (111) and (200) reflections of aluminum with 2.333 and 2.021 A. spacings.

Photographs of our fibers with Ni-filtered CuKα radiation showed equator reflections, which have never been observed in former investigations. Since these reflections were weak and diffuse, depending in some way on the solvent for polyacrylonitrile and on the coagulating bath used, we tried to get more reflections and to get them sharper and stronger by means of the following thermal treatments:

(a) The yarn was wound on a frame, heated in glycerol or in a nitrogen atmosphere for 2 hr. to 180, 190, and 200°C., then slowly cooled

down to 70°C. within 3 hr. The fibers heated in glycerol were washed with methanol. Photographs of the fibers treated at 200°C. showed sharper and more intensive equator reflections, but at 220°C. only an oriented diffuse halo extending from the original innermost to the outermost reflection could be seen.

(b) Another way to increase the intensity and sharpness of the new reflections proved to be treatment of our fibers with mixtures of water and different solvents for polyacrylonitrile such as 30% dimethylsulfoxide, dimethylformamide, ethylene carbonate, or one of the inorganic salt solutions, such as 56.7% $ZnCl_2$ in water, which only swells polyacrylonitrile. Our samples were dipped into these solutions for 30 hr. in a fixed state in order to reach equilibrium between the solvent content in the fiber and in the water. Then the yarn was thermoset at constant length. In this case, the solvent in the fibers acts as a plasticizer and facilitates the formation of an increased lateral order in our fibers depending on the plasticizer in a specific way.

(c) A good means to increase the lateral order of our fibers to get more equatorial reflections was a treatment for 30 hr. in dimethylformamide as in (b) and a periodic stretching and shrinking of the fibers during the thermosetting process at 180°C.

Figure 1 shows the diagram of our fibers treated in such a way. During the thermosetting we stretched the fibers slowly within 60 min. to 5%. In the next 60 min. we relaxed the fibers slowly to the original length and then repeated the stretching process.

TABLE I

Equator Reflections of 1:15 Stretched Polyacrylonitrile Fibers after the Described Treatment of our Fibers According to Fig. 1 and the Text

Name	Intensity*	$\sin\theta$	d,A.
A_1	st	0.1343	5.73
A_2	v st	0.1485	5.18
A_3	w	0.1701	4.52
A_4	st	0.1848	4.16
A_5	v w	0.2002	3.84
A_6	v w	0.2163	3.56
A_7	m	0.2300	3.35
A_8	st	0.2522	3.05
A_9	v w	0.2836	2.71
A_{10}	v w	0.2954	2.60
A_{11}	v w	0.3148	2.44

*st, strong; v st, very strong; w, weak; v w, very weak; m, middle.

Preliminary Results

Table I shows number, intensity, $\sin\theta$, and spacing of all equator reflections of Figure 1. A_1, A_3, A_4, and A_9 have never been observed before according to our knowledge, while A_2, A_7, and A_8 are usually found, and A_6 as well as A_{10} might correspond to very weak reflections in the table of Stefani, Chevreton, Garnier and Eyraud (3).

It may be assumed that the reflections found up to now for polyacrylonitrile fibers, which in most cases were dry-spun, did not allow for any final conclusions on the highest attainable lateral order.

For the appearance of the new reflections found, different reasons can be proposed: First, the wet-spinning process with a high stretching ratio of the fibers in two stages at 170°C., and the special thermal treatment increased by the action of plasticizers leads in every case to the formation of a higher lateral order and more, sharper, and stronger equator reflections of polyacrylonitrile fibers. Second, it is also possible that most investigators used an aperture system of their fiber cameras with too low a resolution for the innermost equator reflections of polyacrylonitrile fibers.

In an early issue of the Journal of Polymer Science an analysis of the lateral order of polyacrylonitrile fibers of the new reflections found will be given in connection with an explanation of the influence of plasticizers and thermal treatments.

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POLYMER NEWS

The Division of High-Polymer Physics of the American Physical Society will hold its Twenty-Third Meeting at St. Louis, Missouri, on March 26-28, 1963, in connection with that of the parent Society during the same week at the same place. Program Chairman is Dr. Fraser P. Price, Research Laboratories, General Electric Co., P. O. Box 1088, Schenectady, New York.

The 14th Annual Mid-America Spectroscopy Symposium which is to be held at the Sheraton-Chicago Hotel in Chicago from May 20-23, 1963, is pleased to announce that the Chicago Gas Chromatography Discussion Group will present their annual Spring program concurrently with the Symposium.

The following is a list of invited Symposium speakers:

NMR
Dr. Roy Bible, G. D. Searle
Dr. Charles Bell, University of Illinois

EPR
John Heise, Chas. F. Kettering Institute

Visible-Ultraviolet
Dr. D. McClure, University of Chicago

Infrared and Raman
Mr. S. Sundaram, Illinois Institute of Technology
Dr. E. R. Lippincott, University of Maryland
Dr. G. Pollack, National Bureau of Standards

Flame
Dr. J. A. Dean, University of Tennessee
Dr. W. A. Cooke, University of Cornell

Emission
Panel Discussion: Mr. A. Goldblatt, Angstrom, Inc.

X-ray
Dr. I. Adler, U. S. Geological Survey
Mr. E. L. Gunn, Humble Oil and Refining Company
Dr. R. H. Munch, Monsanto Chemical Company
Panel Discussion: Mr. V. Buhrke, Picker X-ray Company
Mr. V. Bicks, U. S. Naval Research Laboratories

Gas Chromatography

Mr. R. Juvet, University of Illinois
Dr. H. Syzmanski, Canisius College

The Symposium on Molecular Structure and Spectroscopy will be held at the Department of Physics and Astronomy, The Ohio State University, this year from June 10 to June 14, 1963. There will be discussions of the interpretation of molecular spectroscopic data as well as methods for obtaining such data. In addition, there will be sessions devoted to those phases of spectroscopy of current interest. During this same period the Triple Commission for Spectroscopy will meet at The Ohio State University to discuss its agenda of business and to present a series of invited and contributed papers on atomic and molecular spectroscopy. A dormitory will be available for those who wish to reside on the campus during the meeting. For further information, or for a copy of the program when it becomes available, write to Professor H. H. Nielsen, Department of Physics and Astronomy, The Ohio State University, 174 West 18th Avenue, Columbus 10, Ohio.

Manuscripts should be submitted to one of the members of the Editorial Board or to the Editorial Office, c/o H. Mark, Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn 1, New York. Address all other correspondence to Interscience Publishers, a Division of John Wiley & Sons, Inc., 440 Park Avenue South, New York 16, New York.